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# Monoanionic Dipyrrin–Pyridine Ligands: Synthesis, **Structure and Photophysical Properties**

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A novel monoanionic tetradentate N4 ligand (F<sub>5</sub>DPPy) based on a dipyrromethene skeleton as a molecular platform and decorated with pyridine rings at the 1- and 9-positions of the dipyrrin motif has been prepared and characterized. Interestingly, although this ligand is weakly fluorescent, it presents a chelation-enhanced fluorescence effect of around 150 times upon coordination to Zn<sup>II</sup>. Time-dependent (TD) DFT calculations reproduce nicely the spectroscopic features of both

Introduction

The BODIPY class of dyes has gained much attention since it was recognised that they can be used in a variety of applications such as biological sensing and labelling, in electroluminescent devices and as potential candidates for solid-state solar concentrators, among others.<sup>[1]</sup> Their chemical stability, high molar absorption coefficients and fluorescence quantum yields are among the main assets of this class of dyes. It is noteworthy that the enormous synthetic methodology leading to differently substituted dipyrrinato organic skeletons has also contributed to a large extent to reaching a range of targeted functionalities.<sup>[2]</sup> Dipyrrinbased metal complexes have also been reported; these show decreased emission intensities compared with their corresponding boron-based derivatives. However, recent developments have led to stable luminescent complexes with ap-

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the ligand and the complex, and analysis of the electron density redistribution in the excited state suggests that a better orbital overlap of the HOMO and LUMO in  $F_5DPPyZnCl$ compared with  $F_5DPPy$  is responsible for the more intense transitions observed with the former system. As such, this ligand opens interesting perspectives in the design of ratiometric sensors.

preciable quantum yields.<sup>[3]</sup> The bischelating nature of dipyrrins and the ease with which the meso-position can be functionalized with other coordinating functionalities have been used to develop light-harvesting metal-organic frameworks (MOFs)<sup>[4]</sup> or ytterbium(porphyrinate)-BODIPY conjugates.<sup>[5]</sup>

The dipyrrin backbone also offers another synthetic handle at the carbon 1- and 9-positions (in the  $\alpha$ -positions of the pyrrolic rings) for the addition of ligating groups, thereby generating novel pseudo-macrocyclic ligands. Following this strategy, new scaffolds bearing amido,<sup>[6,7]</sup> imino<sup>[7,8]</sup> and phenolate<sup>[9]</sup> moieties have been synthesized and coordinated to various transition-metal and/or group 13 ions. The fluorescent properties of a p-iodophenyl-dipyrrinphenol boronate derivative was reported by Burgess and co-workers, which gave a quantum yield of 0.41 in chloroform.<sup>[9b]</sup> Nabeshima et al. described a mesityl-dipyrrinphenol aluminate adduct that can be additionally coordinated through the oxygen atoms of the phenolate groups to a zinc ion, thus enhancing the fluorescence yield of the initial species from  $\Phi_{\rm F} = 0.72$  to 0.83 in toluene/ MeOH.<sup>[9c]</sup> It has to be noted though, that the lability of the zinc ion in the latter heteronuclear complex requires the presence of a large excess of ZnCl2 under micromolar concentrations. All these above-mentioned studies support the primary interest in developing novel ligand scaffolds that ultimately permit the deployment of coordination chemistry for material science objectives.<sup>[10]</sup> In our group, we have been interested in using the dipyrrin core as a molecular platform to develop a new N4 tetracoordinating cavity. We describe, herein, the synthesis of a monoanionic ligand

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where we have introduced two 2-pyridyl groups at the 1and 9-positions of the dipyrrin motif. To the best of our knowledge, this synthetic scaffold can only be found in rare examples of expanded porphyrin analogues bearing substituents in the  $\beta$ , $\beta'$ -positions,<sup>[11]</sup> and only one coordination chemistry study was described for the case of a labile dinuclear Co<sup>II</sup>–pyriporphyrin complex.<sup>[12]</sup> Interestingly, although our ligand is weakly fluorescent, it presents a chelation-enhanced fluorescence effect of around 150 times upon coordination to Zn<sup>II</sup>.

#### **Results and Discussion**

The synthetic route to the monoanionic dipyrromethenedipyridine ligand (DPPy) is described in Scheme 1. Suzuki coupling of *N*-Boc (*tert*-butyloxycarbonyl) protected (2pyrrolyl)boronic acid to 1-bromopyridine in the presence of  $[Pd(PPh_3)_4]$  and  $K_2CO_3$  followed by acid deprotection afforded 2-(2-pyrrolyl)pyridine in 77% yield. Condensation of 2 equiv. of the pyrrole with 1 equiv. of pentafluorobenzaldehyde in the presence of *p*-toluenesulfonic acid (*p*-TSA) followed by treatment with 2,3-dichloro-5,6-dicyano-1,4benzoquinone (DDQ) allowed the desired ligand to be isolated in 46% yield over two steps.



Scheme 1. Synthesis of  $F_5DPPy$  and its related complexes: (i) Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, 2-bromopyridine, THF, 100 °C, 18 h, 55%; (ii) HCl, CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O, 0 °C, 24 h, 99% ; (iii) pentafluorobenzaldehyde, *p*-TSA, toluene/C<sub>2</sub>Cl<sub>4</sub>, 123 °C, 7 d, 46%; (iv) DDQ, THF/ CHCl<sub>3</sub>, room temperature, 5 h, 99%; (v) **5**: ZnCl<sub>2</sub>, NEt<sub>3</sub>, THF, 30 min, 96%; **6**: Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O, toluene, 110 °C, 12 h, 98%.

Single crystals of sufficient quality for X-ray analysis were obtained from a saturated diethyl ether solution. X-ray crystallography analysis revealed that the molecule is almost planar with the two ancillary pyridine N atoms only slightly deviating from the dipyrrin average plane (p) (N4– p 0.14 Å, N3–p 0.01 Å). Notably, the pyridyl N2 atom points in the opposite direction to the coordinating cavity and the perfluorinated phenyl ring is flipped by 63.5° from the ligand backbone plane (Figure 1).



Figure 1. Front and side views of the X-ray crystal structure of ligand  $F_5DPPy$  and complex  $F_5DPPyZn$ . Protons and solvent molecules are omitted for clarity.

Complexation of the ligand to zinc chloride in THF occurs rapidly in the presence of triethylamine. The <sup>1</sup>H NMR spectrum reveals the disappearance of the NH signal and a shift of the aromatic proton signals. To determine the coordination mode of the complex in the solid state, single crystals of sufficient quality were grown from a saturated diethyl ether solution, and the complex structure was determined by single-crystal X-ray diffraction analysis (Figure 1). The metal atom is tetracoordinated by the four nitrogen atoms, which supports the fact that the N2-containing pyridine ring rotates to bind the metal atom inside the predefined N4 coordinating cavity. One chloride ion as an exogenous ligand completes the coordination sphere. The Zn atom adopts a quasi-square-pyramidal geometry with a deviation of 0.50 Å from the N4 plane. No noticeable differentiation is observed within the C-N or the C-C bonds of the two rings of the dipyrromethene backbone (see the Supporting Information), thus suggesting a delocalization of the electron density.

The electrochemical properties of the free ligand were studied by cyclic voltammetry. On the cathodic side of the cyclic voltammogram a quasi-reversible one-electron reduction wave was observed at -0.88 V versus a saturated

calomel electrode (SCE;  $\Delta E = 137$  mV; Figure 2), accounting for the formation of a rather stable radical anion, the stability of which is probably due to the presence of the electron-withdrawing perfluorinated phenyl ring. On the anodic side, an irreversible oxidation process was noted at 1.4 V. Upon addition of a solution of ZnCl<sub>2</sub>/NEt<sub>3</sub>, the cathodic wave disappeared, and a new reversible process appeared at -0.68 V versus SCE ( $\Delta E = 144$  mV; Figure 2). Given the silent redox nature of the Zn<sup>II</sup> ion, this new wave was attributed to ligand reduction, which became easier upon complexation. The cyclic voltammogram of



Figure 2. Cyclic voltammograms of a solution of  $F_5DPPy$  (2 mM) in THF/tBu<sub>4</sub>NPF<sub>6</sub> (0.1 M) (red), upon addition of 0.5 equiv. (purple) and 1 equiv. (blue) of (ZnCl<sub>2</sub>, 1.5 NEt<sub>3</sub>). v = 100 mV s<sup>-1</sup>, potential recorded vs. SCE.

 $F_5$ DPPyZnCl was recorded separately and confirmed this hypothesis (see the Supporting Information).

Interestingly, a colour change from red to fluorescing deep blue was observed in solution upon addition of zinc chloride to F<sub>5</sub>DPPy, suggesting a marked modification of the optical properties of the ligand upon coordination. Accordingly, monitoring of the formation of the complex by absorption spectroscopy revealed a 92 nm bathochromic shift of the spectrum in the visible range as shown by the decrease in the absorption band at  $\lambda_{max} = 511 \text{ nm}$  ( $\varepsilon =$ 17000 Lmol<sup>-1</sup> cm<sup>-1</sup>) along with the concomitant appearance of a double-hump band at  $\lambda_{1,\text{max}} = 603 \text{ nm}, \lambda_2 =$ 563 nm ( $\varepsilon_1 = 13700 \text{ Lmol}^{-1} \text{ cm}^{-1}$ ,  $\varepsilon_2 = 32600 \text{ Lmol}^{-1} \text{ cm}^{-1}$ ; Figure 3). To evaluate the suitability of  $F_5DDPy$  for use as a fluorescent sensor, emission spectra were also recorded. As expected, the ligand is poorly fluorescent ( $\lambda_{exc} = 511$  nm,  $\lambda_{\Phi} = 580$  nm,  $\Phi_{\rm F} = 0.002$ ) with a Stokes shift (S) of 69 nm. Upon coordination, the zinc complex exhibits a strong emission at 620 nm ( $\lambda_{exc} = 603$  nm,  $\Phi_{F} = 0.31$ , S = 17 nm). No such effect was observed with other metals, such as nickel (see the Supporting Information), as previously observed for other systems.<sup>[13]</sup> Although the ligand is a modest fluorescent probe, such a remarkable chelation-enhanced fluorescence (CHEF) effect could allow its use as a ratiometric sensor. As a comparison, complexation of Zn<sup>2+</sup> to a dipyrromethene-diphenolate analogue only led to a threefold increase in emission with a bathochromic shift of 15 nm.<sup>[11]</sup>

To interpret such an enhancement in the fluorescence properties of the tetradentate N4 ligand, theoretical calculations were performed. The geometry of the two molecules was optimized by density functional theory (DFT) methods, and the predicted structures compare reasonably well with the experimental ones (Figure S5 in the Supporting



Figure 3. (a) UV/Vis spectra of  $F_5DDPy$  in acetonitrile (13  $\mu$ M) upon addition of 0–1 equiv. of ZnCl<sub>2</sub>·1.5NEt<sub>3</sub>. (b) Emission spectra in acetonitrile (1.5  $\mu$ M).



Information). Inspection of their respective highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) shows that both are delocalized  $\pi$ -orbitals, which are distributed over the dipyrrin-pyridine ligand (Figures S6 and S7 in the Supporting Information). Evaluation of the HOMO-LUMO gap of both F<sub>5</sub>DPPy and F<sub>5</sub>DPPyZnCl reveals a shift of approximately 0.1 eV (Table S2 in the Supporting Information), indicating that  $F_5$ DPPyZnCl can be more easily reduced than  $F_5$ DPPy in agreement with the previous cyclic voltammetry study. The optical properties of both the free ligand and the corresponding zinc derivative were investigated by using timedependent density functional theory (TD-DFT). Our calculations adequately reproduce the key features of the experimental UV/Vis spectra of F<sub>5</sub>DPPy and F<sub>5</sub>DPPyZnCl; namely, the two bands at 511 and 603 nm (calculated as 511 and 556 nm, respectively) and the observed bathochromic shift (Figure 4). Based upon the TD-DFT results, the electronic transitions responsible for the prominent UV/Vis transitions can be described as HOMO-LUMO transitions (Tables S3 and S4 in the Supporting Information). Consistent with the experimental results, TD-DFT predicts that the extinction coefficient for the complex is approximately 1.5 times larger than that of the ligand.



Figure 4. Predicted UV/Vis spectra (curves) and corresponding electronic transitions (sticks) of  $F_5DPPy$  and  $F_5DPPyZnCl$ .

One way to visualize the electron-density redistribution in the excited state is a difference electron density plot (Figure 5, Figures S8 and S9 in the Supporting Information). This plot shows that the UV/Vis transition in F<sub>5</sub>DPPy has significant charge-transfer character with electron density being donated by one pyrrin–pyridine unit to the other. In contrast, the UV/Vis transition in F<sub>5</sub>DPPyZnCl may be better described as a  $\pi$ - $\pi$ \* one with electron density being transferred within the ligand backbone. Such analysis is consistent with the compositions of the MOs involved in these transitions. Consequently, we can suggest that the better orbital overlap of the HOMO and LUMO in F<sub>5</sub>DPPyZnCl compared with F<sub>5</sub>DPPy is responsible for the more intense UV/Vis transition observed with the former

system. The structures of the two molecules were then optimized in the first excited state by using TD-DFT methods to extract fluorescence emission wavelengths. The results of these calculations give an emission wavelength of 558 and 583 nm for F<sub>5</sub>DPPy and F<sub>5</sub>DPPyZnCl, respectively (observed: 580 and 620 nm, respectively). A detailed structural analysis of the changes implied by the S0 $\rightarrow$ S1 transition in both systems helps to shed some light on the difference between the two emission wavelengths. We observe that fewer bonds are affected by the excitation within the F<sub>5</sub>DPPy framework of the complex compared with that of the ligand (Figure S5 in the Supporting Information), which would explain the bathochromic shift observed between these two species. The values of the calculated oscillator strengths (0.705 and 0.314, respectively) confirm that  $F_5DPPyZnCl$  is a much more fluorescent species than F<sub>5</sub>DPPy, as observed experimentally. This difference is also consistent with the fact that the complex originally features a better HOMO-LUMO overlapping volume, which was suggested to be a factor of fluorescence enhancement and higher light emission efficiency.<sup>[14]</sup>



Figure 5. Difference electron density sketches of the main UV/Vis transitions for  $F_5DPPy$  (left) and  $F_5DPPyZnCl$  (right) (yellow = negative, red = positive).

### Conclusion

We have reported the synthesis of a novel monoanionic tetradentate N4 ligand based on a dipyrrin platform. We have found that this ligand is weakly fluorescent, but upon chelation with zinc(II) a noticeable increase of about 150 times is observed. As such, this new ligand may give new possibilities to optimize the optical properties through different substitution patterns. Moreover, this ligand offers a new coordination set to develop metal complexes for the activation of small molecules. Efforts are currently being conducted in this direction.

### **Experimental Section**

**General Procedures and Materials:** All commercially available compounds were used as received except for pentafluorobenzaldehyde, which was freshly distilled prior to use. (*N*-Boc-2-pyrrolyl)boronic acid was synthesized according to a literature procedure, and its deprotection was performed according to a standard procedure.<sup>[15]</sup>



Tetrahydrofuran was dried by distillation from sodium/benzophenone. Chromatography was performed with Merck silica gel 60 (230–400 mesh). NMR spectroscopy chemical shifts ( $\delta$ ) are given in ppm relative to the residual solvent signal and using hexafluorobenzene ( $\delta = -164.9$  ppm vs. CFCl<sub>3</sub>) as an internal standard for <sup>19</sup>F NMR spectroscopy. Peak multiplicities are designated by the following abbreviations: s (singlet), d (doublet), t (triplet), m (multiplet), br. (broad), p (pseudo), and coupling constants (*J*) are provided in Hertz (Hz). CCDC-1400703 (for 3) and -1400704 (for 4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request/cif.

2-(N-Boc-1H-pyrrol-2-yl)pyridine (1): (N-Boc-2-pyrrolyl)boronic acid (250 mg, 1.18 mmol, 1 equiv.) and 2-bromopyridine (112.5 µL, 1.18 mmol, 1 equiv.) were dissolved in tetrahydrofuran (10 mL) and added to [Pd(PPh<sub>3</sub>)<sub>4</sub>] (138 mg, 1.19 mmol, 0.1 equiv.) under argon. Aqueous K<sub>2</sub>CO<sub>3</sub> (3 mL, 1.2 M) was then added, and the biphasic mixture was stirred vigorously and heated at 100 °C for 18 h. After cooling to room temperature, water (150 mL) was added to the reaction mixture, and the aqueous phase was extracted with dichloromethane ( $4 \times 50$  mL). The combined organic extracts were washed with brine (50 mL), then dried with MgSO<sub>4</sub>, filtered, and concentrated. The resulting crude orange oil was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, 9:1) to yield 1 as a yellow oil (195 mg, 78%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz):  $\delta$  = 1.36 (s, 9 H, CH<sub>3</sub>), 6.25 (t, J = 3.3 Hz, 1 H), 6.42 (dd, J = 3.3, 1.8 Hz, 1 H), 7.20 (ddd, J = 12, 4.8, 1.2 Hz, 1 H),7.36–7.43 (m, 2 H), 7.68 (td, J = 7.5, 1.8 Hz, 1 H), 8.60–8.64 (m, 1 H) ppm.

**2-(2-Pyrrolyl)pyridine (2):** Compound **1** (1.27 g, 5.22 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, and aqueous HCl (28.5 mL, 3 M) was added dropwise at 0 °C. The biphasic mixture was vigorously stirred at room temperature overnight. The aqueous solution was separated from the organic phase and basified (pH = 12) with aqueous Na<sub>2</sub>CO<sub>3</sub>, then extracted with dichloromethane. The combined organic phases were dried with MgSO<sub>4</sub> and filtered. The solution was concentrated, and ethyl acetate was added in the same proportion as dichloromethane. Filtration of the red solution through an alumina pad afforded a colourless solution that was concentrated to dryness to give **3** as a brown solid (750 mg, 99%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 360 MHz):  $\delta = 6.30$  (dt, J = 2.6, 3.6 Hz, 1 H), 6.7 (m, 1 H), 6.9 (m, 2 H), 7.03 (dd, J = 2.0, 5.5 Hz, 1 H), 7.54 (d, J = 7.7 Hz, 2 H), 7.62 (td, J = 7.7, 1.6 Hz, 1 H), 8.45 (d, J = 5 Hz, 1 H), 9.8 (br. s, NH) ppm.

Dipyrromethane 3: Compound 2 (249 mg, 1.73 mmol, 2 equiv.) was dissolved in toluene/tetrachloroethane (1:1; 30 mL) and added to p-TSA (498 mg, 2.60 mmol, 3 equiv.) and pentafluorobenzaldehyde (104 µL, 868 µmol, 1 equiv.) in toluene (15 mL). The mixture was heated at reflux under argon for 7 d, after which it was basified to pH = 12 with aqueous  $K_2CO_3$  (1 M). The aqueous phase was extracted with dichloromethane, and the combined organic phases were dried with MgSO<sub>4</sub>, filtered, and the solvents evaporated to dryness to give 3 as a brown solid (370 mg, 0.79 mmol, 46%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  = 5.90 (s, 1 H, H<sub>ipso</sub>), 6.12 (br. s, 2 H, H<sub>pyrrol</sub>), 6.63 (br. s, 2 H, H<sub>pyrrol</sub>), 7.01 (t, *J* = 5.9 Hz, 2 H, H<sub>pyridyl</sub>), 7.52 (m, 4 H,  $H_{pyridyl}$ ), 8.38 (d, J = 4.7 Hz, 2 H,  $H_{pyridyl}$ ), 9.74 (br. s, 2 H, NH) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 63 MHz):  $\delta$  = 33.59 (C-H), 111.06 (C-H<sub>pyrrol</sub>), 112.22 (C-H<sub>pyridyl</sub>), 119.92 (C-H<sub>pyrrol</sub>), 120.67 (C-H<sub>pyridyl</sub>), 125.96 (C-H<sub>pyridyl</sub>), 127.68 (C-F), 128.98 (C-H<sub>pyridyl</sub>), 134.33 (C<sub>q</sub>), 139.96 (C<sub>q</sub>), 141.40 (C-F), 144.84 (C<sub>q</sub>), 147.80 (C-F) ppm. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 235 MHz):  $\delta = -144.43$  (dd, J = 21.6,

6.9 Hz, 2 F,  $F_{ortho}$ ), -158.64 (pt, J = 21.6 Hz, 1 F,  $F_{para}$ ), -164.29 (pdt, J = 21.6, 6.9 Hz, 2 F,  $F_{meta}$ ) ppm. ESI<sup>+</sup>-HRMS: calcd. for  $C_{25}H_{16}F_5N_4$  [MH<sup>+</sup>] 467.1290; found 467.1278.

F<sub>5</sub>DPPyH (4): A solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (270 mg, 1.19 mmol, 1.5 equiv.) in tetrahydrofuran (50 mL) was added dropwise to dipyrromethane 3 (378 mg, 0.81 mmol, 1 equiv.) in chloroform (80 mL) at room temperature over 30 min. The dark-red mixture was stirred for 5 h, and the solvents were evaporated to dryness. The residue was dissolved in dichloromethane and washed with aqueous  $K_2CO_3$  (1 M; 500 mL). The aqueous solution was extracted with dichloromethane, and the combined organic phases were dried with MgSO<sub>4</sub>, filtered, and the solvents evaporated to dryness to give 4 as a red solid (374 mg, 0.81 mmol, 99%). Single crystals were obtained by slow solvent evaporation from a saturated diethyl ether solution. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz):  $\delta$  = 6.59 (d, J = 4.4 Hz, 2 H, H<sub>pyrrol</sub>), 7.10 (d, J = 4.4 Hz, 2 H, H<sub>pyrrol</sub>), 7.29 (m, 2 H), 7.82 (dd, J = 7.8, 1.6 Hz, 2 H), 8.20 (d, J = 8.1 Hz, 2 H), 8.72 (d, J = 4.7 Hz, 2 H), 13.70 (br. s, 1 H, NH) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 63 MHz):  $\delta$  = 118.2 (C-H<sub>pyrrol</sub>), 121.6 (C-H<sub>pyridyl</sub>), 122.5 (C<sub>q</sub>), 123.5 (C-H<sub>pyridyl</sub>), 128.1 (C-H<sub>pyrrol</sub>), 135.9 (C-F), 136.8 (C-H<sub>pyridyl</sub>), 139.8 (C-F), 142.2 (C<sub>q</sub>), 143.1 (C<sub>q</sub>), 147.1 (C-F), 150.0 (C-H<sub>pyridyl</sub>), 151.0 (C<sub>q</sub>), 156.0 (C<sub>q</sub>) ppm. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 235 MHz):  $\delta = -142.12$  (m, 2 F, F<sub>ortho</sub>), -156.16 (pt, J = 21.3 Hz, 1 F,  $F_{para}$ ), -163.83 (m, 2 F,  $F_{meta}$ ) ppm. ESI<sup>+</sup>-HRMS: calcd. for  $C_{25}H_{14}F_5N_4$  [MH<sup>+</sup>] 465.1133; found 465.1116.  $C_{25}H_{14}F_5N_4$  (465.4): calcd. C 64.66, H 2.82, N 12.06; found C 64.72, H 2.83, N 12.03. UV/Vis (CH<sub>3</sub>CN): λ<sub>max</sub> = 511 nm;  $\varepsilon = 17000 \text{ Lmol}^{-1} \text{ cm}^{-1}.$ 

**F<sub>5</sub>DPPyZnCl (5):** Triethylamine (21 μL, 150 μmol, 1.5 equiv.) and ZnCl<sub>2</sub> in diethyl ether (1 м, 100 μL, 100 μmol, 1 equiv.) were added to compound **4** (46.4 mg, 100 μmol, 1 equiv.) in acetonitrile (20 mL) at room temperature. The dark-blue solution was stirred for 30 min, then concentrated under reduced pressure. The green/ blue residue was washed with water (10 mL) to give **5** as a blue solid (54 mg, 96 μmol, 96%). Single crystals were obtained by slow solvent evaporation from a saturated diethyl ether/methanol mixture. <sup>1</sup>H NMR [(CD<sub>3</sub>)<sub>2</sub>CO, 250 MHz]: δ = 7.02 (d, *J* = 4.5 Hz, 1 H), 7.11 (d, *J* = 5 Hz, 1 H), 7.64 (dt, *J* = 5.5, 2.5 Hz, 1 H), 8.14 (m, 2 H), 9.10 (d, *J* = 5 Hz, 1 H) ppm. ESI<sup>+</sup>-HRMS: calcd. for C<sub>25</sub>H<sub>12</sub>ClF<sub>5</sub>N<sub>4</sub>NaZn [MNa<sup>+</sup>] 584.9854; found 584.9844. UV/Vis (CH<sub>3</sub>CN): λ<sub>max</sub> = 603 nm; ε = 13700 Lmol<sup>-1</sup> cm<sup>-1</sup>.

**Physical Measurements:** NMR spectra were recorded in the solvent indicated with Bruker DPX250, AVX300, AVX360 spectrometers. High-resolution mass spectrometric data were obtained with a microTOF-Q II, Bruker Compass. UV/Vis steady-state absorption spectra were recorded with a Varian Cary 5000 spectrometer. Steady-state fluorescence spectra were recorded with a Horiba Fluoromax-4 or a Hitachi F-4500 fluorescence spectrophotometer, and laser-flash-induced fluorescence was recorded with an Edinburgh LP920 laser flash photolysis spectrometer. All experiments were performed in sealed quartz cuvettes with samples being purged with argon for 15 min before the experiments. The absolute yields were determined with Rhodamin 6G ( $\lambda_{exc} = 480$  nm) and Cresyl Violet perchlorate ( $\lambda_{exc} = 550$  nm) as standards for the ligand and the complex, respectively.

**Electrochemical Experiments:** Cyclovoltammetry was conducted under argon by using a PGSTAT 302 potentiostat and a threeelectrode cell using a saturated calomel electrode as a reference electrode, a Pt counter electrode, and a carefully polished glassy carbon disk electrode as the working electrode.

Computational Details: All theoretical calculations were based on density functional theory (DFT) and were performed with the



ORCA program package.<sup>[16]</sup> Full geometry optimizations were carried out for all complexes by using the hybrid functional B3LYP<sup>[17]</sup> in combination with the TZV/P<sup>[18]</sup> basis set for all atoms and by taking advantage of the resolution-of-the-identity (RI) approximation in the Split-RI-J variant<sup>[19]</sup> with the appropriate Coulomb fitting sets.<sup>[20]</sup> Increased integration grids (Grid4 in ORCA convention) and tight SCF convergence criteria were used. Vibrational frequency calculations were performed to ensure that each geometry optimization converged to a real minimum. Solvent effects were accounted for according to the experimental conditions. For that purpose, we used acetonitrile as the solvent ( $\varepsilon = 9.08$ ) within the framework of the conductor-like screening (COSMO) dielectriccontinuum approach.<sup>[21]</sup> Vertical electronic transitions and dipole moments were calculated by using time-dependent DFT (TD-DFT)<sup>[22]</sup> within the Tamm–Dancoff approximation.<sup>[23]</sup> To increase computational efficiency, the RI approximation<sup>[24]</sup> was used in calculating the Coulomb term, and at least 40 excited states were calculated in each case. Difference transition density plots were generated for each transition and visualized with the Chemcraft program.<sup>[25]</sup> Excited-state geometry optimizations were performed in the absence of symmetry constrains making use of analytic gradients, as implemented for the TD-DFT method in the ORCA program package.<sup>[26]</sup> Fluorescence electronic transitions were calculated as vertical de-excitations based on the TD-DFT-optimized geometries of the first excited state.

**Supporting Information** (see footnote on the first page of this article):  $F_5DPPyZnOAc$  synthesis, NMR spectra, crystallographic data, additional photophysics studies and computational details.

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